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Chemistry of intermediate layer water-oil emulsion formation

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Abstract. The paper considers the problem of accumulation and disposal of oil sludge including a resistant water-oil emulsion, oil sludge classification and treatment methods are presented. Detailed studies have revealed that stability giving to the emulsion system consisting of two immiscible liquids requires presence of the third component which performs function of a stabilizer. These stabilizers create boundary adsorption films which are a structural and mechanical barrier to contact and coalescence dispersed water globules. The structure of intermediate layer and lower sublayer is considered, the reasons for their formation are determined.

Currently, all the oil sludge is accumulated at oil fields, and then disposed of by incineration in specialized installations. In turn, tank oil sludge includes a stable water-oil emulsion, which can be separated for further oil and water use. This is a more environmentally friendly method for processing and disposing of oil sludge waste. Therefore, it becomes relevant to study and develop possible methods of persistent water-oil emulsions destruction that will allow more efficient use of tank waste and reduce the total amount of oil sludge burned [1].

Taking into account all the variety of different oil wastes characteristics all oil sludge can be divided into three main groups in accordance with their formation conditions, namely groundwater, near-bottom and tank sludge types.

The first ones are formed as a result of petroleum products spills into the soil during production operations, or in emergency situations. Near-bottom sludge is formed when oil settles at the bottom of water bodies, and tank type sludge is deposited during oil products storage and transportation in tanks of different designs.

In its simplest form, oil sludge is a multicomponent stable aggregative physicochemical systems consisting mainly of oil products, water, and mineral additives (sand, clay, metal oxides, etc.).

The main reason for tank sludge formation is the physicochemical petroleum products interaction in a specific oil receiving plant with moisture, air oxygen and mechanical impurities, as well as with the material of tank walls. All this leads to water-oil emulsions and mineral dispersions formation.

In fact, it is known that water and oil often form a hard-to-separate oil emulsion. It is formed during watery oil recovery, in oil field pipelines, as well as in oil desalting plants due to intense turbulent oil-water emulsion mixing. At the same time, on the phase boundary surfaces there has been an accumulation of natural emulsifiers (asphaltenes, naphthenes, resins, paraffins, salts, etc.) contained in produced fluid, which in turn contribute to emulsion stabilization.

Emulsions stability depends on the following factors:



- average diameter of water globules: the smaller globule diameter is, the slower globule will settle in the oil mass and the more stable the emulsion will be;
- emulsion "life" time: the more time has passed since the formation of emulsion, the thicker the solvation layer is;
- nature of hydrodynamic effects on the flow of oil: the more of them, the smaller diameter of the droplets, that is, the more stable the emulsion is;
- physicochemical oil properties and chemical composition of the emulsified water, since deposition rate of droplets under equal conditions depends on oil density: the more oil density, the lower sedimentation rate of particles is;
- emulsion temperature, it determines oil density and viscosity: the composition and thickness of solvation layer around water globules change with increasing temperature.

When settling oil-water emulsions in the tanks of primary crude oil distillation units (CODU), so-called "intermediate layers" are formed between the separated layers of free oil and water. High stability of such emulsions creates special difficulties in the process of sludge treatment.

Data analysis in sci-tech literary studies and a long-term practice allow us to single out the following basic methods for the disposal of oil sludge: thermal, mechanical, chemical.

The simplest mechanical method is gravitational settling in large-capacity vessels, where oil resides for 1-2 hours. The method is inefficient and almost never used in its pure form.

Due to oil emulsions destruction as a result of chemical reagents use, natural emulsifiers and stabilizers are displaced from the protective layer into oil or water phase. At the same time, they can be dissolved or be in a colloid-dispersed state. As a result of selective action of demulsifiers used, some stabilizers (natural surfactants) are displaced from reservation shells surface into oil volume, transforming into a dissolved state, while others are transferred to aqueous or oil phase, wetting, becoming hydrophobic or becoming hydrophilic. The accumulation of natural stabilizers at the interface is also a source of intermediate layers' formation [2].

Complex technology contributes to deeper purification and includes a combination of several methods. At the moment, such method of oil sludge disposal as burning or accumulating at landfill areas is common in oil and gas industry. However, these methods have a negative impact on the environment and thus, there is no possibility of oil sludge components secondary use [3].

In view of insufficiently studied intermediate layers' structure, composition and properties as well as their formation mechanisms, today it is difficult to identify an effective method for separating intermediate layer oil-water emulsions.

Therefore, the primary aim of the research was to consider the chemistry of intermediate layer water-oil emulsion formation.

There are a number of general theories explaining the emergence of stable emulsion systems, which can be conventionally divided into thermodynamic (energy) and supramolecular, associated with the formation of a structural-mechanical barrier. All these theories are unanimous in that in order to impart stability to an emulsion system consisting of two immiscible liquids; the presence of the third component is necessary, which performs the function of a stabilizer.

The main natural stabilizers are: asphalt-resin substances, porphyrin complexes, high-melting paraffins, mineral particles (clay, silt, sand, insoluble salts). These stabilizers provide boundary adsorption films, which are the structural-mechanical barrier to the contact and coalescence of dispersed water globules [4].

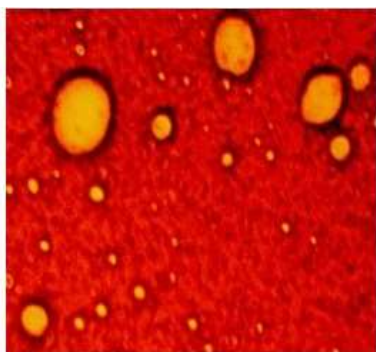


Figure 1. Micrographics of an intermediate layer emulsion.

The intermediate layer is a multiple emulsion which is water globules surrounded by particles of emulsion stabilizers adsorbed on them. The intermediate layer consists of two highly watered layers of inverse and direct emulsions, separated by the interfacial contact surface of oil-water dispersion medium.

When entering the processing plant, incoming inverse oil emulsion is crushed in the aqueous phase, with the formation of large drops of oil with droplet water in them, which quickly float and are retained by a dense layer that has not had time to coalesce with drops of oil. Large local formation of oil with droplet water in them, remaining in the aqueous medium, form lower sublayer of direct multiple emulsion, the boundary from the aqueous phase forms lower boundary of the intermediate layer. A layer of inverse emulsion containing small water globules forms upper sublayer, the boundary from the oil phase forms upper boundary of the intermediate layer.

Lower sublayer is the zone of the most concentrated emulsion and compacted packaging of globules, the volume does not exceed 10% of the total height of the intermediate layer and water content reaches 40-60%. It is in this layer the emulsion is divided into separate phases as a result of intensive coalescence of droplets with the aqueous phase and interdrop coalescence.

Upper sublayer, in which for lower boundary the water content varies from 30% to 60%, at upper boundary there is a sharp decrease in the water content to the value of initial emulsion. In this sublayer, coalescence of some droplets can occur and their size increases to a critical value at which they are able to precipitate out in a countercurrent of the dispersed phase.

The intermediate layer will increase until the amount of water entering into its upper part per unit of time is equal to the amount of water coalescing on the interfacial surface. In the case of a low water cut due to large distance between the globules and low density of the intermediate layer, the inter-drop coalescence and coalescence of the globules with the interfacial surface is low.

As a result, the height of the intermediate layer increases. In the case of a high water cut of raw material, critical size of the globules increases, which also leads to an increase in the height of the intermediate layer. If the intermediate layer thickness is 0.5 m, transition of the water globules into the layer of commercial water stops completely [5].

During oil emulsions separation paraffin microcrystals, asphaltenes and resins are concentrated on the interfacial surface in capacitive equipment. The main amount of mechanical impurities is also concentrated at the interface, where the accumulation of the main volumes of the most stable oil emulsions with incompletely destroyed reservation shells of water globules occurs.

Insufficient demulsifier amount in oil emulsion is the cause of incomplete destruction of water globules reservation shells and an increase in aggregate and kinetic emulsion stability. On the other hand, when the concentration in the oil demulsifier emulsion is higher than optimal, the formation and increase in the number of gel structure associates occurs, leading to improved emulsion stability.

The formation of intermediate layers occurs due to the action of dynamic factors — presence of an equal ratio of volume fractions of water and oil (an average microemulsion phase) containing predominantly water globules less than 10 μm in size that penetrate the entire volume of upper layer of the aqueous phase and lower layer of the oil phase. The formation of such emulsion structure is associated with phase transformations in resin-asphaltenes subsystem and formation of colloidal

structures as a result of strong interaction. This is confirmed by recorded anomalous density values, which are observed when the water content is 45–55%; when relative volumes of dispersed and dispersive phases are approximately equal [6].

Environmental pollution by oil and oil products is one of the most intense and dangerous human environmental impacts. Virtually the entire chain, starting with exploration and ending up with the use of petroleum products, is associated with the formation of oil wastes.

In addition, it is estimated that every year oil enterprises in Russia make up about 600 thousand tons of oil sludge, and the world total volume is 6 million tons.

The wastes that occur while working with oil products are the most dangerous pollutants. Oil sludge pollutes air, vegetation and soil, groundwater.

The Russian Federation is the state that is leading in terms of the amount of refining and oil production, so there is a lot of sludge that need to be disposed of. 4 – 8% of oil products are lost in the form of contamination at any stages of the process.

But, despite a significant amount of waste, in our country rational methods for sludge processing are still poorly developed. Low-cost disposal options are most commonly used in Russia: waste incineration and disposal, which negatively affects human health and environment.

Due to adverse effect of oil sludge on the environment the question concerning the basic reasons for the emergence of intermediate layer highly stable emulsion is rated as a highly relevant issue.

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